Modelling the effect of Ni coarsening on the anodic three phase boundary and electrical conductivity of SOFCs with infiltrated anodes*

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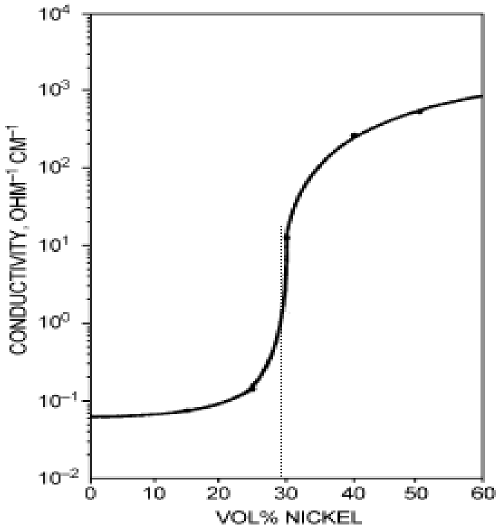
**, Work initiated at IIT Delhi, ca. 2008; re-visited*

Work initiated, ca. 2007-08, IIT D

DST (Govt of India) Sponsored Project, 2008-10

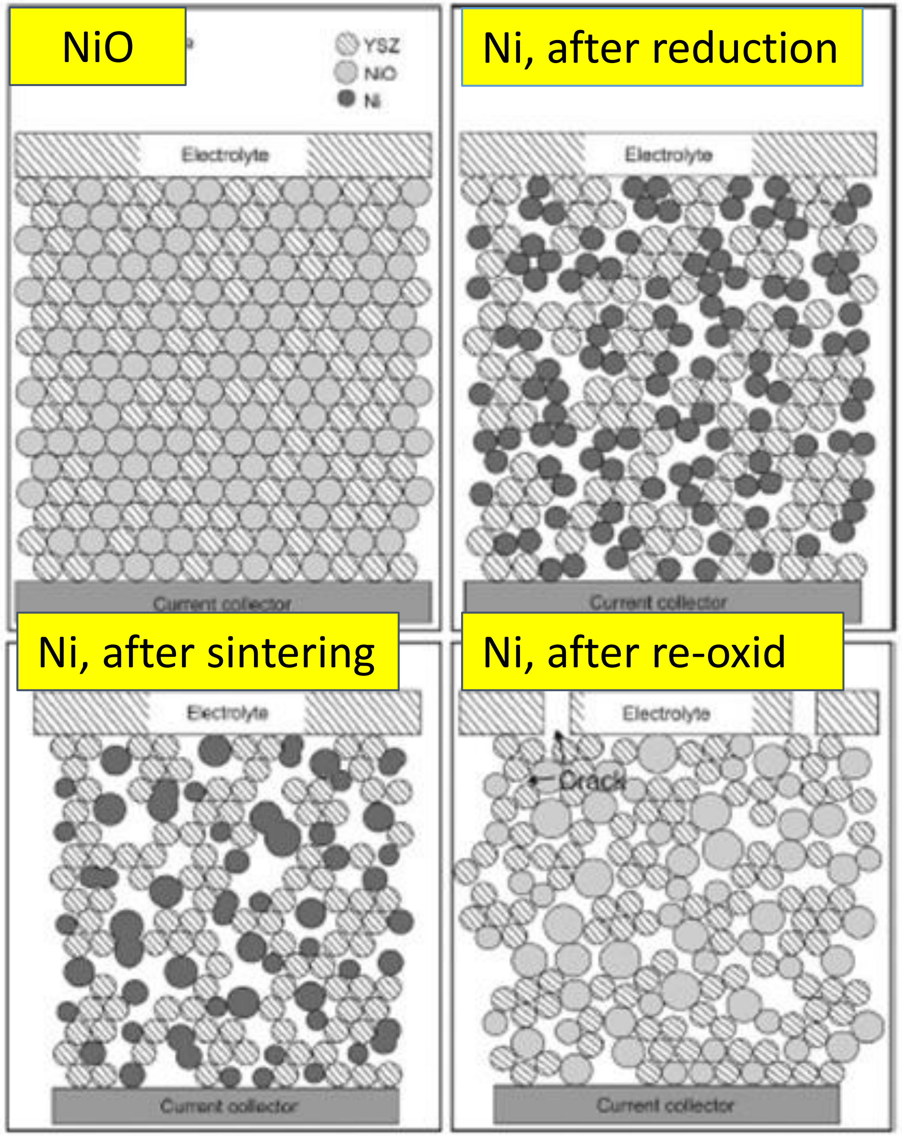
- **Exploration of Infiltration of Ni in anodes, as opposed to NiO-YSZ cermets**
- **One of the recurrent problems – Redox Stability, at the required high Ni loadings**



Dees et al., J. Electrochem. Soc. 134(9) (1987) 2141.

High Ni loadings exacerbate Redox failure

Proposed Mechanism of Redox Failure[1]



NiO

Ni, after reduction

Ni, after sintering

Ni, after re-oxid

1. *Klemenso et al., J. Electrochem. Soc. 152(11) (2005) A2186.*

Reducing Ni content in anodes – lot of work in this area, 2000-10

- **Liquid dispersion technique[1]**
- **Electroless coating technique[1]**

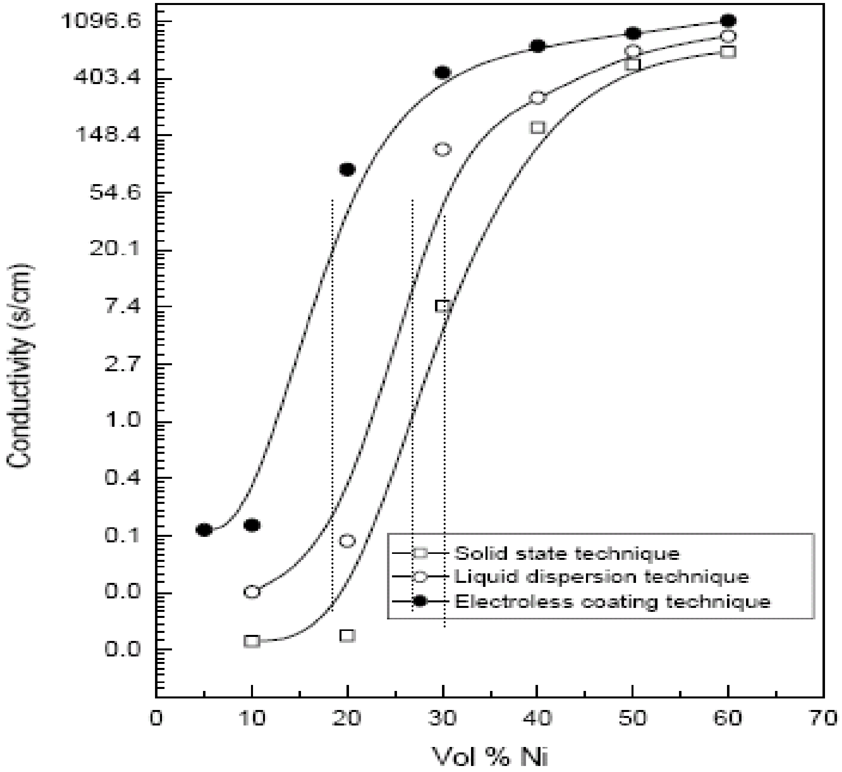


Fig . Conductivity as a function of Ni vol% and fabrication technique

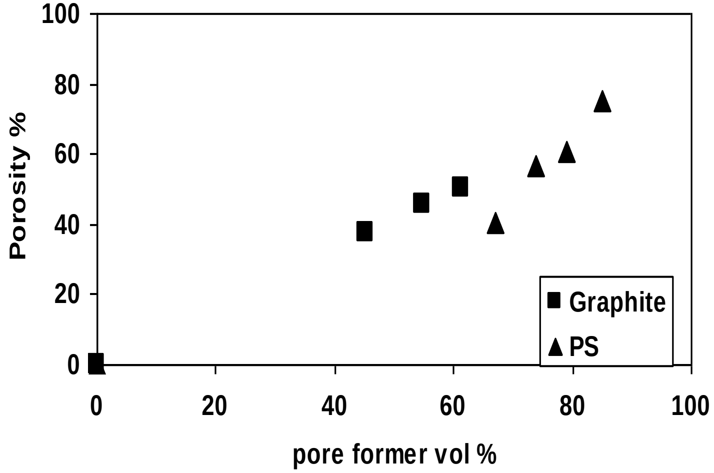
1. *Pratihar et al., MRS Bull. (2005), 40*
2. *Craciun et al., J Electrochem. Soc. 146(11) (1999) 4019.*
3. *Tucker et al., J. Power Sources, 171 (2007) 477*
4. *Busawon et al., Solid. St. Lett. 11(10) (2008) B186*
5. *Qiao et al., J. Power Sources, 169(2) (2007) 253*

Impregnation / infiltration into porous pre-forms/ scaffolds

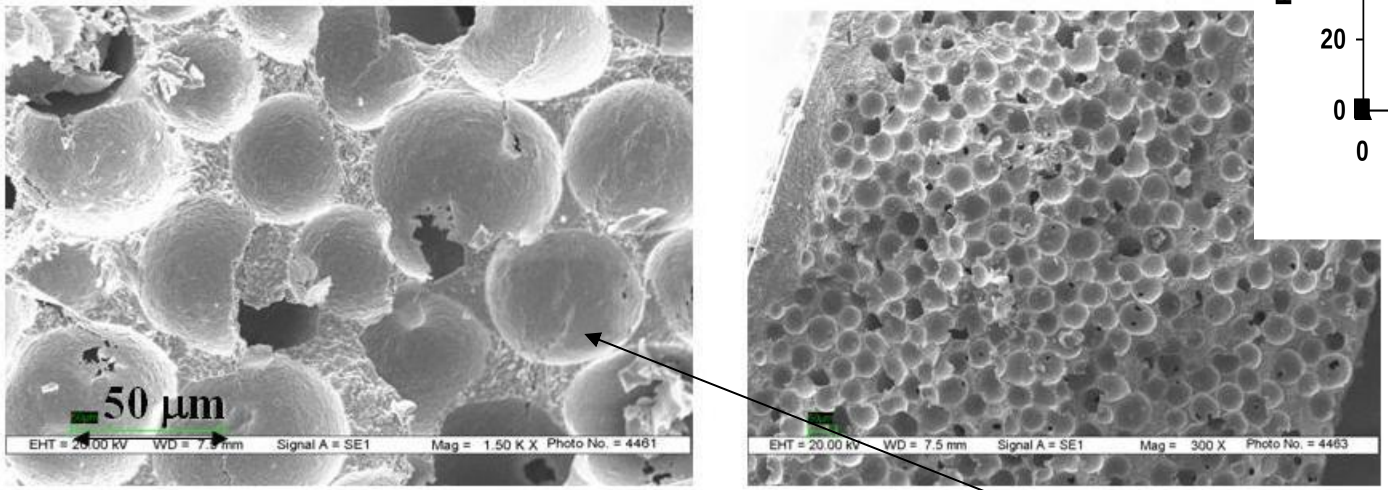
- ***Gorte et al*[2] - Cu/CeO2/YSZ**
  - **agglomeration of the Cu particles above 700 C – sintering, loss of contact at TPB**
- ***Visco et al*[3] - Ni impregnation in metal supported anodes . Cells show redox tolerance for 5 redox cycles.**
  - **agglomeration of the Ni particles above 700 C – sintering, loss of contact at TPB and rapid performance losses initially.**
- ***Atkinson et al*[4] – Study of redox behavior of Ni impregnated anodes.**
- ***Qiao et al*[5] – Ni-CeO$_2$ impregnation in porous YSZ substrate.**

Morphology of anode substrates prior to impregnation – function of pore-formers

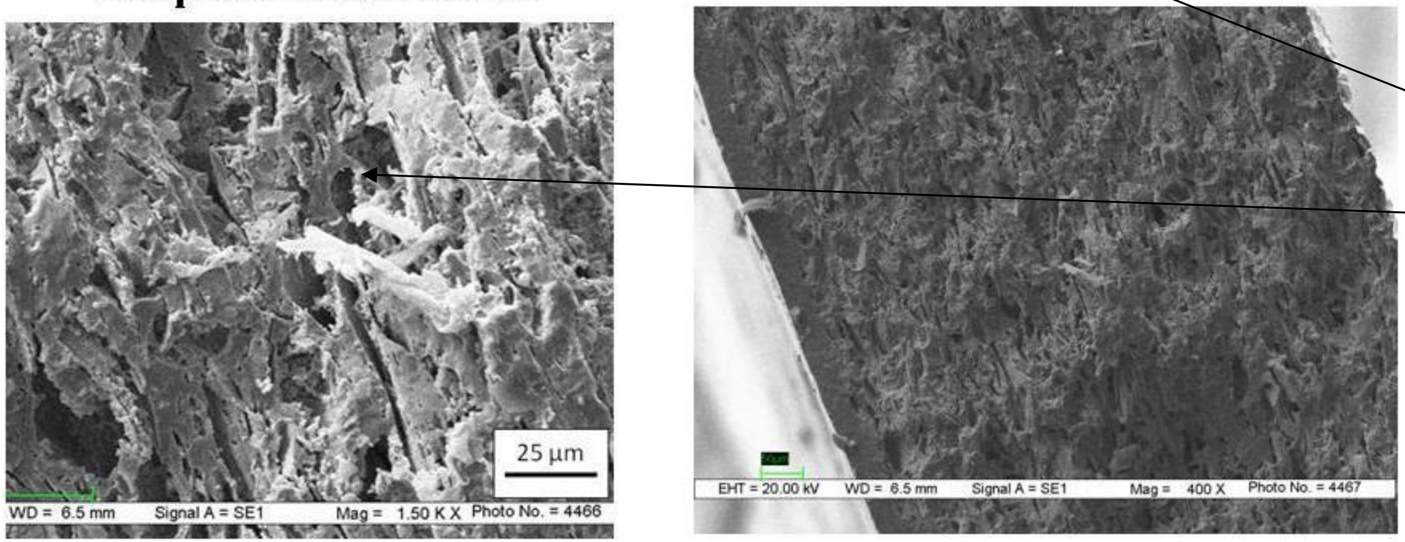
Other substrates tried out – starch, needle coke



Polystyrene based anode



Graphite based anode



Pore Size

>20 µm

1 -2 µm

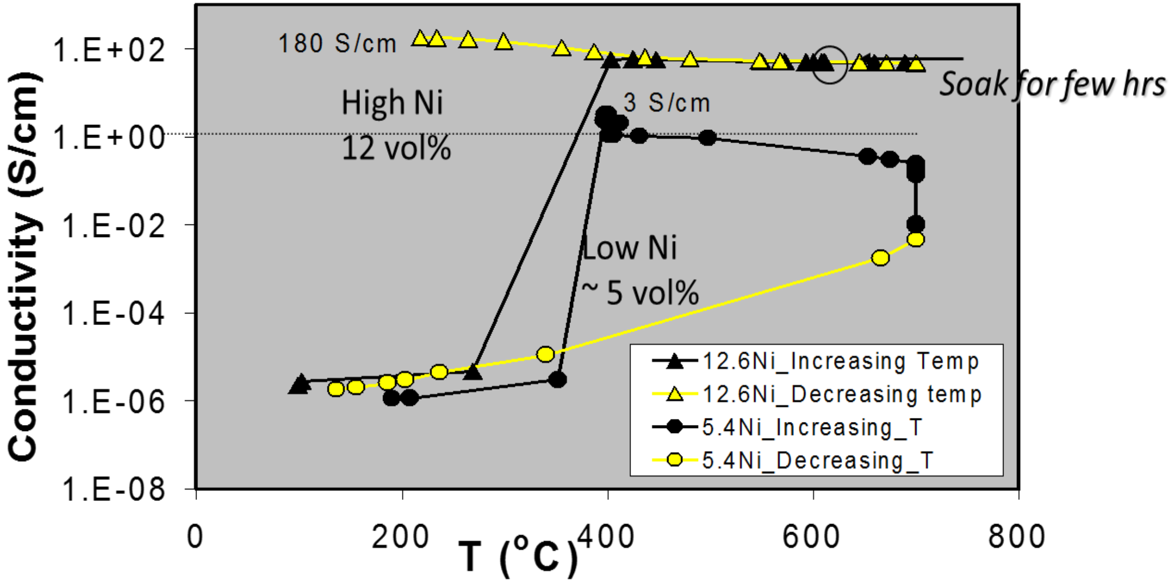
Porosity

35 – 60%

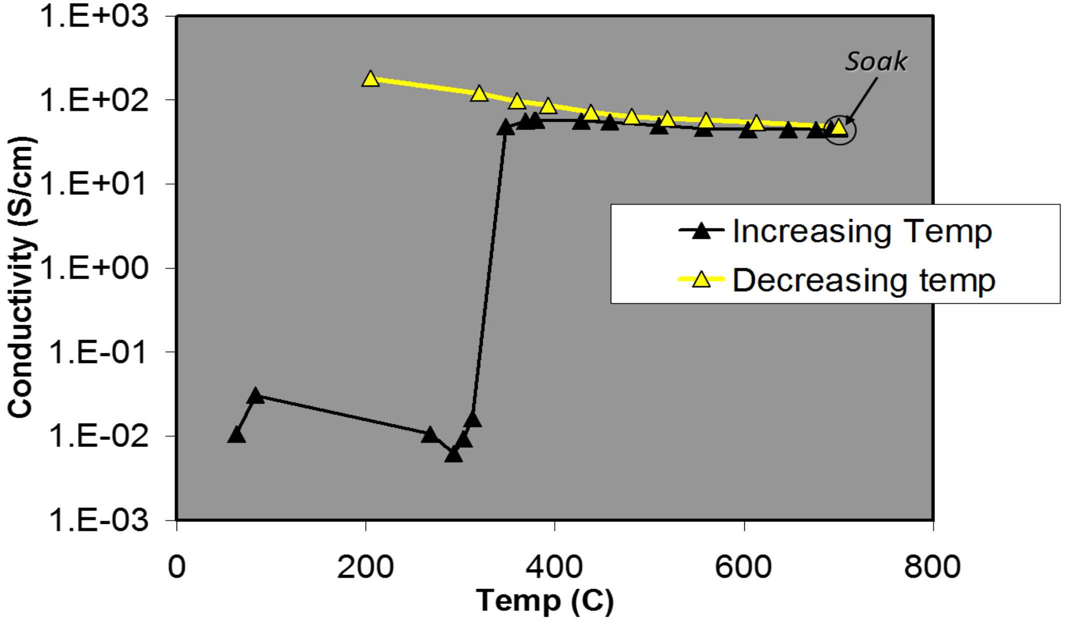
Tortuosity

And back in 2008-10, we showed - Conductivity of Ni-YSZ porous slabs as function of Temperature and Time (Ni infiltrated via NiNO3 solution precursor on to pre-formed porous YSZ scaffold)

Case – Ni-YSZ prepared using Polystyrene pore-formers – porosity of 60%



Confirmation of stability of Ni at higher loadings, i.e., above 10 Vol %
(starch being pore former, here, 45 % porosity)



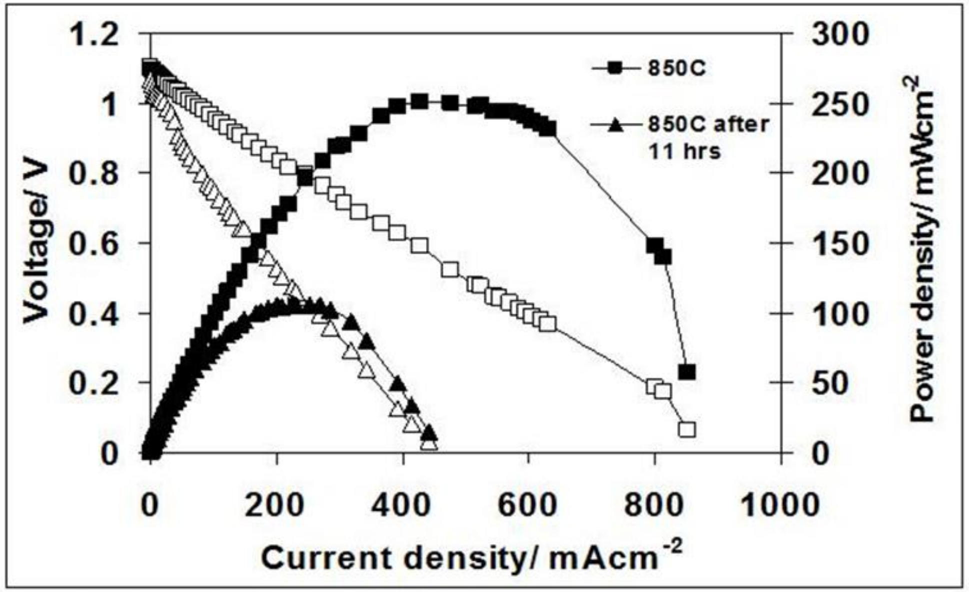
<u>At low Ni concentrations</u>

Drop in metallic conductivity at 700°C upon soaking, to pure YSZ levels; Ionic behavior/ not Ni (Arrhenius dependency with T)

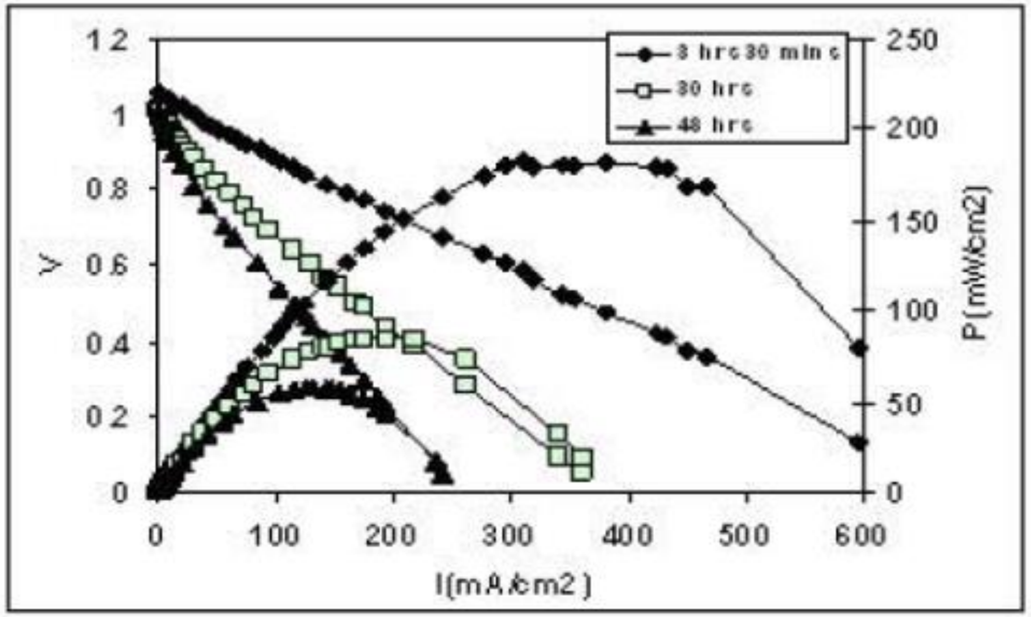
Ni is effectively disconnected, due to sintering

Stable conductivity at 12 Vol. % Ni-YSZ loadings !!!

Ni-infiltrated cells work, but performance deactivates with time – shown in 2 examples



57% porosity; 11 Vol % Ni



Performance degrades as time progresses

References:

Ph.D. Thesis of C. Anand Singh (IITD, 2009)

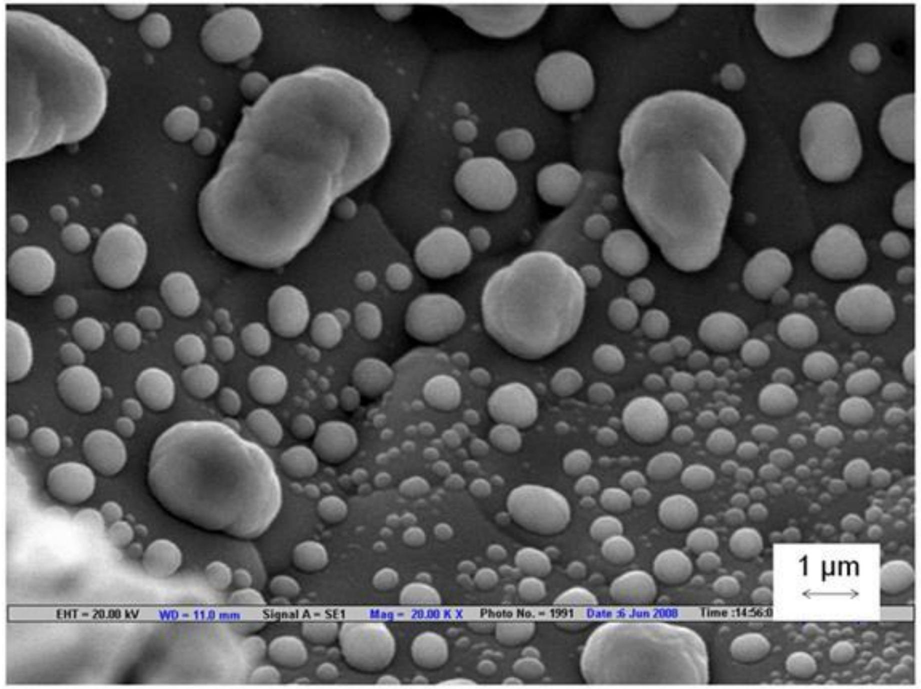
Strong Metal Support Interactions (SMSI) Of Infiltrated Ni With TiO_2 In A Porous YSZ Anode Matrix – A Possible Method For Ni-stabilization; C. A. Singh, L. Bansal, P. Tiwari and **V. V. Krishnan; ECS Transactions 25(2), 1897-1904 (2009).**

Synthesis and Characterization of Ni-impregnated Porous YSZ anodes for SOFCs; C. Anand Singh and **Venkatesan V. Krishnan**; **Advances in Solid Oxide Fuel Cells IV, 173 – 179, Copyright © 2009 The American Ceramic Society**.

Anode Characterization and SOFC Performance using Ni-YSZ anodes formed by Ni-impregnation methods; C. Anand Singh and **Venkatesan V. Krishnan**; **ECS Transactions 6 (21) 25-32 (2008)**

Effect of operating temperature on thermal stability

SEM after 10 hours



SEM after 100 hours

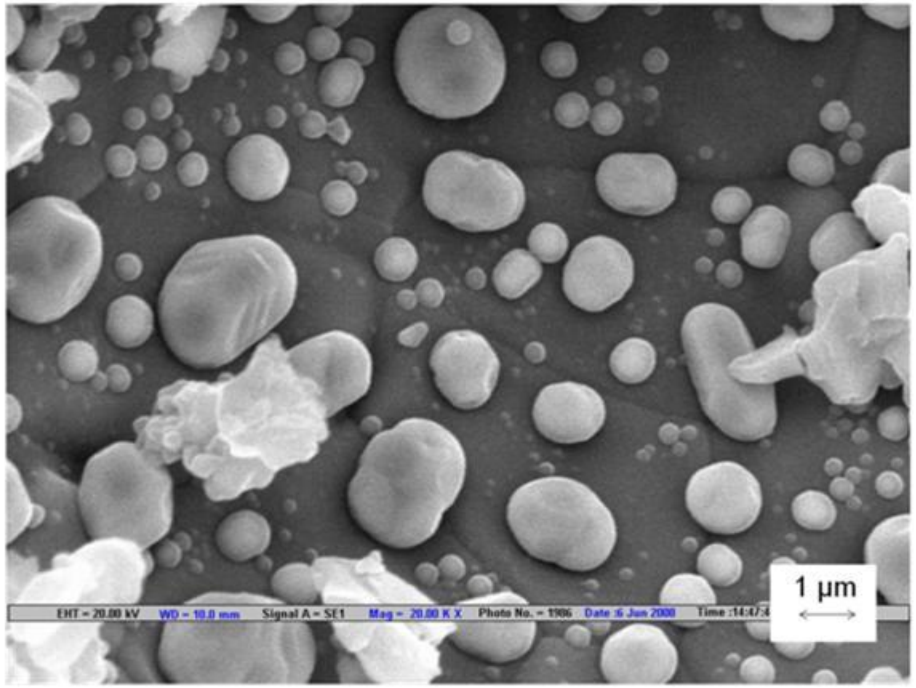


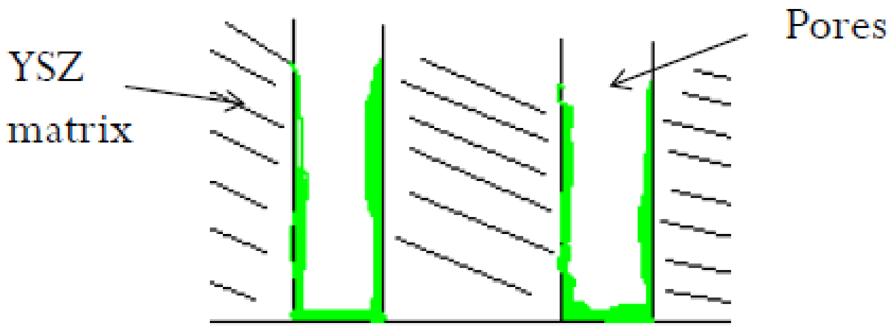
Fig. SEM images of polystyrene induced pore of anodes after operation for (a) 10 h and (b) 100 h 20kX Magnification

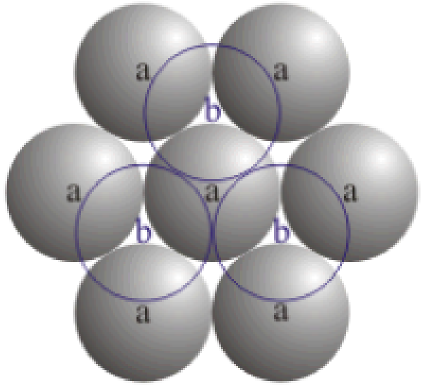
- The Ni particles grow in size due to sintering at 800^{o}C for long durations.
- Poor wetting of Ni on the YSZ surface
- Initial particle size growth is highest → maximum degradation in the first 10 hours
- Lowering of connectivity between Ni particles → lower electronic conductivity …. Or so one would think!!!
- **BUT, if conductivity is stable, Why is performance going down??**

First point: How to evaluate 3 phase boundary length of Infiltrated Ni particles in a porous pre-form?

Basic Approach Followed → A cylindrical pore/ parallel pore model (Wheeler), where we introduce the concept of tortuosity

- Cylindrical and parallel pore model proposed by Wheeler has been assumed. The pores are considered to be cylindrical and parallel. [4]
- Nickel particles are assumed to be rigid spheres in hexagonal closed packing





We do assume that there are significant numbers of Ni particles, and that the porous surface is fully covered

- The average pore length is defined with the help of a parameter called tortuosity factor τ. $x_L = \tau L$, where x_L gives the tortuous length of pore cylinders and L is the actual thickness of electrode.

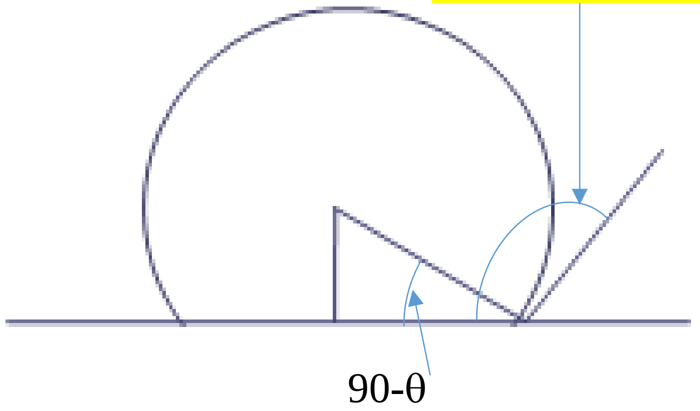
ESTIMATE OF INITIAL TRIPLE PHASE BOUNDARY LENGTH (contd.)

- Total Number of pores per unit volume of anode

$$N_{pores} = \frac{porosity}{Vol_{onepore}} = \frac{\varepsilon_p}{\pi \frac{d_{pore}^2}{4} l_{pore}} = \frac{\varepsilon_p}{\pi \frac{d_{pore}^2}{4} (\tau L)}$$

Schematic of Ni Particle on surface

Contact angle: θ = 117°, for Ni



- NICKEL DEPOSITION ON BASE OF PORES:
- For monolayer deposition, volume of the layer is given by:

$$V_{monolayer} = \pi \frac{d_{pore}^2}{4} d_{Ni}$$

- Assuming a packing efficiency of 0.72 (based on volume), the number of nickel particles deposited on pore base per pore:

$$N_{Ni} = \frac{0.72 V_{monolayer}}{V_{Ni-particle}} = \frac{0.72\pi \frac{d_{pore}^2}{4} d_{Ni}}{\pi \frac{d_{Ni}^3}{6}}$$

- NICKEL DEPOSITION ON LATERAL SURFACE AREA OF PORES:
  - Using a similar approach, nickel particles deposited on lateral surface area of a pore can be given by

$$N_{Ni} = \frac{0.72 V_{monolayer}}{V_{Ni-particle}} = \frac{0.72(\pi d_{pore} L\tau) d_{Ni}}{\pi \frac{d_{Ni}^3}{6}}$$

3 phase boundary region – No. of Ni particles can change with d_{Ni} particle size → l_{tpb} can be per volume; based on N_{pores} (also per unit volume)

$$l_{tpb} = N_{pores} N_{Ni} [\pi d_{Ni} \sin\theta]$$

$$l_{tpb} = N_{pores} N_{Ni} [\pi d_{Ni} \sin\theta] \qquad \ldots\ldots\ldots\ldots\ldots 1$$

Where θ is the contact angle between Nickel and YSZ (~117°C)

In addition, if we assume that the triple phase boundary associated with the ‘reaction zone’, is present only at the anode-electrolyte interface, i.e., that the entire reaction takes place at the interface, we can derive the following expression for triple phase boundary.

$$TPBd = f(\varepsilon, \tau, L, d_p, d_{Ni}, \theta_{Ni-YSZ}) = \frac{k'\varepsilon}{4\tau L} \qquad \ldots\ldots\ldots\ldots\ldots 2$$

Where k’ is a constant dependent on the cell materials.

The important feature of the approach is that in a more extensive treatment of this problem, the reaction zone can be extended over the entire anode volume rather than being limited to the anode-electrolyte interface. Accordingly, the TPBD at x = 0 (anode-electrolyte interface) may be given by Equation 2, whereas at all x > 0 up to x = L, the total value is given by Equation 3.

$$TPBLd = f(\varepsilon, \tau, L, d_p, d_{Ni}, \theta_{Ni-YSZ}) = k\varepsilon \left[\frac{1}{4\tau L} + \frac{1}{d_p} \right] \qquad \ldots\ldots\ldots\ldots\ldots 3$$

To be used only, once you are away from the interface

MODELS FOR SINTERING

Sehested, J., 2003., *Journal of Catalysis* , 217(1), pp. 417-426.
Sehested, J. et al., 2004.. *Journal of Catalysis,* 223(1), pp. 432-443.

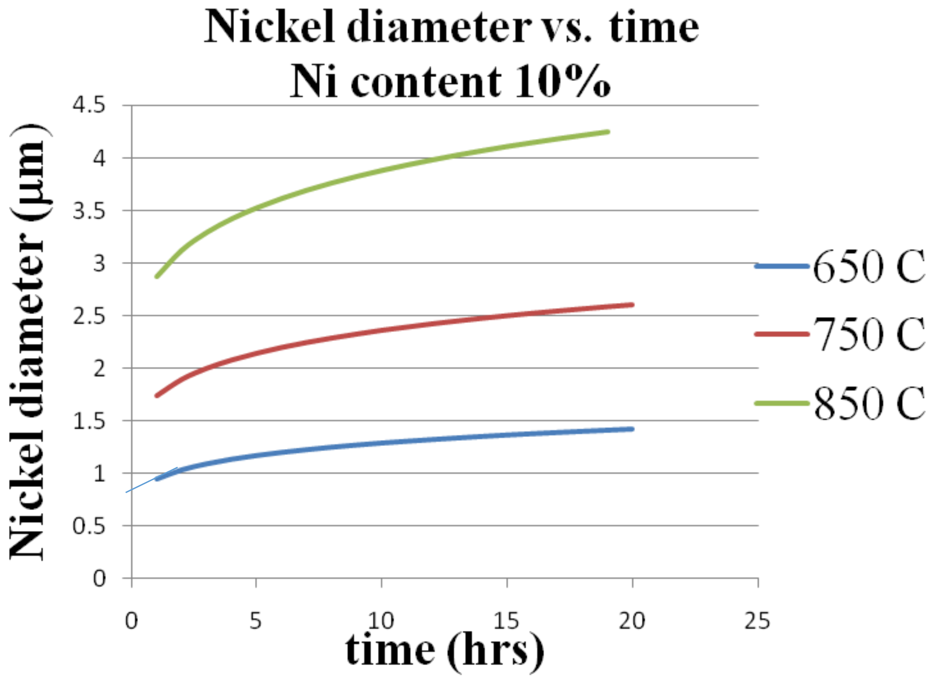
- Rate of sintering of metal particles on ceramic support is fast at first and later reaches an almost stable level. This can be mathematically described by a power law model.

- The temporal evolution of the average nickel particle diameter according to

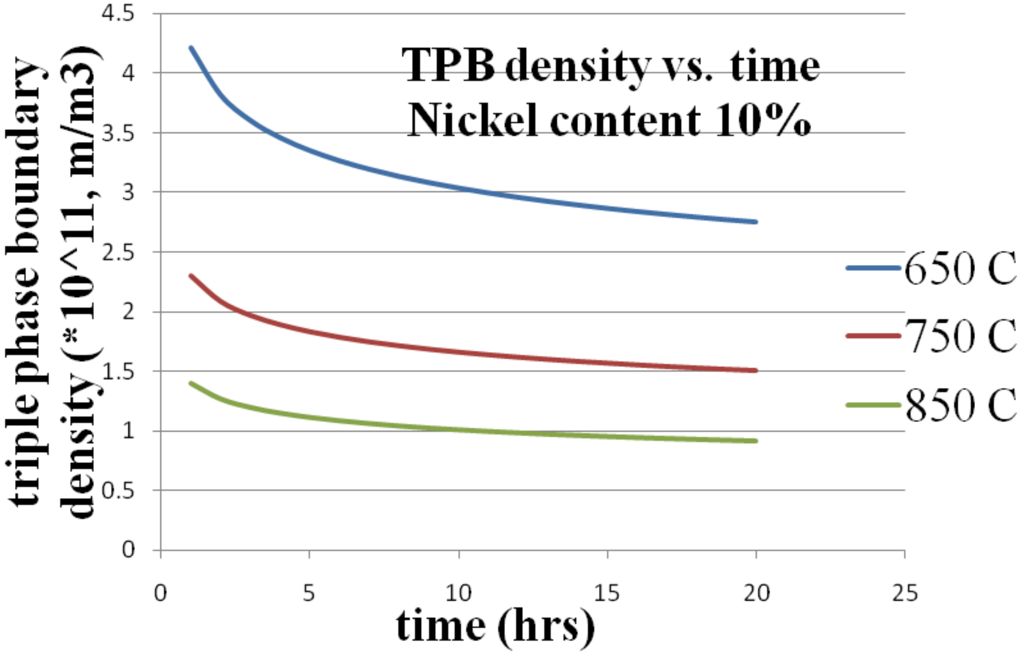
$$\frac{d(d_{Ni})}{dt} = A\frac{X_{Ni}}{(1 - X_{Ni})A_{ysz}d_{Ni}^{6}}\left(\frac{p_{H_2O}}{{p_{H_2}}^{0.5}}\right)e^{\frac{-E_a}{RT}}$$

‘t’ - the ageing time
X_{Ni} and A_{YSZ} - the nickel weight fraction and the carrier surface area per gram of carrier
$d_{Ni,o}$ is the average nickel particle diameter for the fresh catalyst, upon immediate reduction
E_a is the activation energy of the sintering process
A is a temperature-independent pre-exponential factor
P_{H2O} and P_{H2} are the partial pressures of steam and hydrogen
The values of a and E^a are $2*10^{-27}$ and 332kJ/mol respectively.

Simulation Results:



EFFECT OF SINTERING ON Ni DIAMETER AND ON TBP



Utilization of Butler Volmer Equation for describing Charge Transfer

$$j = j_0\left[e^{\left(\frac{\alpha n F \eta}{RT}\right)} - e^{\left(\frac{-(1-\alpha) n F \eta}{RT}\right)}\right]$$

- j_0 : exchange current density
- α : charge transfer coefficient
- Electrode half reactions: considering hydrogen as fuel

$CATHODE : \frac{1}{2}O_2 + 2e^{-} \rightarrow O^{2-} ; ANODE : H_2 + O^{2-} \rightarrow H_2O + 2e^{-}$

- Using:
  - $\alpha = 0.5$ [1]
  - $n = 2$

$$\eta_{act} = \frac{RT}{F}\sinh^{-1}\left(\frac{j}{2j_0}\right)$$

In addition to concentration, Temperature, there is linear dependency on 3 phase boundary

Adding the 3-phase boundary component here

$$j_0 = l_{tpb} f(c_r, c_p)\exp\left[-\frac{A}{T}\right]$$

Kinetics

- The rate determining step for the electrochemical oxidation of hydrogen is:

$$H_{ads} + OH^{-}_{ads'} \rightarrow H_2O_{ads'} + e^{-} + (Ni)$$

$$r_3 = k_3\theta_H\theta_{OH} - k_{-3}\theta_{H_2O}(1-\theta_H) \qquad [mol/m.s]$$

$$k_3 = 6\times10^4 \exp\left(\frac{-22251.62}{T}\right)$$

$$k_{-3} = 6\times10^4 \exp\left(\frac{-16029.59}{T}\right)$$

- Recasting the rate in terms of lineal current density (A/m):

$$j_{0'} = 2Fk_3\theta_H\theta_{OH}$$

$$j_{0'} = 2F * 6\times10^4 \exp\left(\frac{-22251.62}{T}\right)\theta_H\theta_{OH}$$

Where θ_H and θ_{OH} are functions of partial pressures of hydrogen and water and equilibrium constants of reaction steps

ADSORPTION

$$H_2(g) + 2(Ni) \rightarrow 2H_{ads}$$

$$r_1 = k_1(1-\theta_H)^2 p_{H_2} - k_{-1}\theta_H^2$$

SURFACE – REACTIONS

$$H_{ads} + O^{2-}_{ads'} \rightarrow OH^{-}_{ads'} + e^{-} + (Ni)$$

$$r_2 = k_2\theta_H\theta_O - k_{-2}\theta_{OH}(1-\theta_H)$$

$$H_{ads} + OH^{-}_{ads'} \rightarrow H_2O_{ads'} + e^{-} + (Ni)$$

$$r_3 = k_3\theta_H\theta_{OH} - k_{-3}\theta_{H_2O}(1-\theta_H)$$

DESORPTION

$$H_2O_{ads'} \rightarrow H_2O(g) + (YSZ)$$

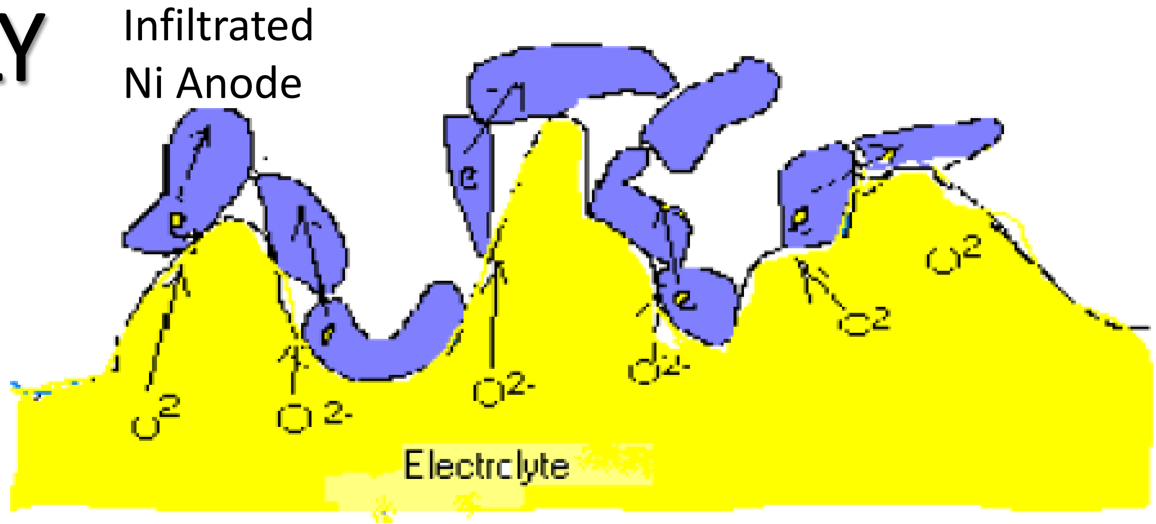
$$r_4 = k_4\theta_{H_2O} - k_{-4}(1-\theta_{H_2O}-\theta_O-\theta_{OH})p_{H_2O}$$

TRANSFER

$$O^{2-}_{bulk} + (YSZ) \rightarrow O^{2-}_{ads'} + lattice vacancy$$

$$r_5 = k_5(1-\theta_{H_2O}-\theta_O-\theta_{OH})c - k_{-5}\theta_O$$

Active TPB AT INTERFACE ONLY

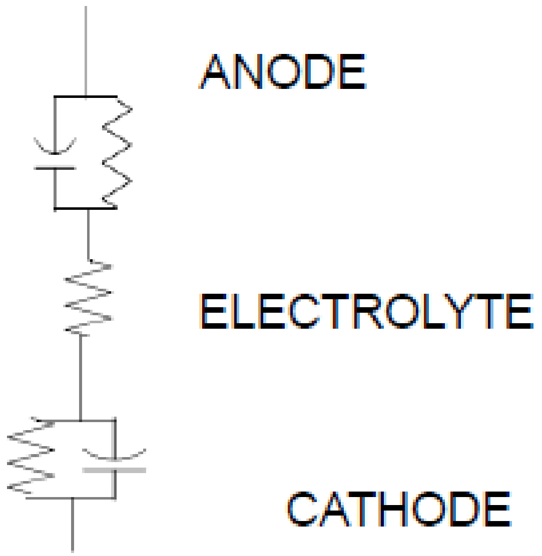


- Cathodic Loss: $\eta = \frac{RT}{F}\sinh^{-1}\left(\frac{j}{2j_0}\right)$
- Electrolytic Loss: $h_{ohmic} = IR_{electrolyte}$
- Anodic Loss: $h_{activation:x=0,anode} = \left[\frac{RT}{F}\sinh^{-1}\left(\frac{j_e}{2j_{0'}l_{tpb}}\right)\right]$

$$h_{ohmic-e,anode} = - i_e \mathrm{R_e}$$

$$ltpb = f(e,t,L,d_p,d_{Ni},q_{Ni-YSZ}) = \frac{k'e}{4tL}$$

- Cell Voltage:



$$V_L = E_{Nernst} - (h_{cathode} + IR_{electrolyte}) - h_{activation:x=0,anode} - h_{ohmic-e,anode}$$

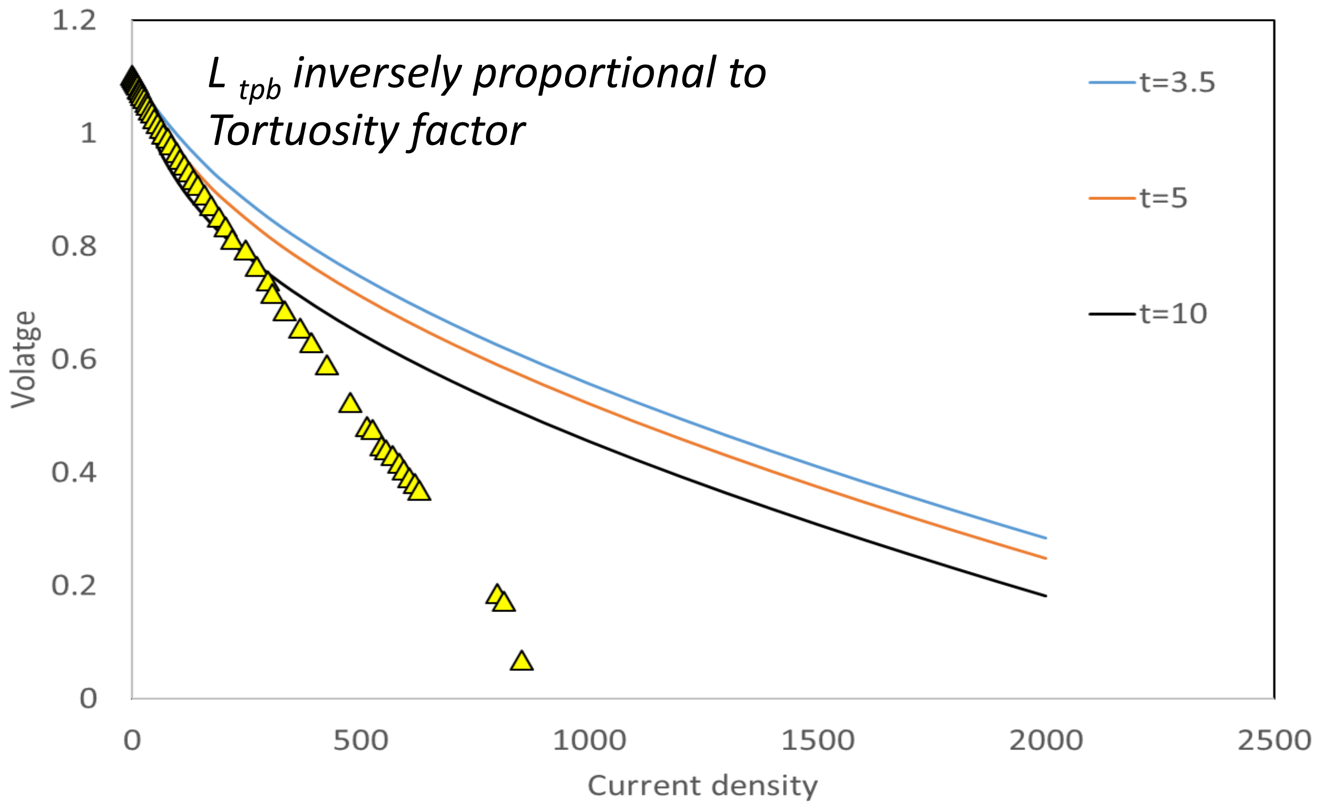
The Charge Carrier in the bulk of the anode is primarily the electron; R_e can be estimated by approximate data from experiment (try values 50-200 S/cm)

Modelling the I-V curves by considering Butler Volmer Kinetics at the Anode-Electrolyte interface ONLY

Parameters		Units
Length of anode	0.0007	m
Porosity	0.57	
Tortosity	3.5	
Diameter of pore	0.00002	m
Length of electrolyte	0.00005	m
Area of cell	0.00005	m2
Theta	2.041	radians
Initial Diameter of Nickel particle	**0.0000002**	m
Volume fraction of Nickel	0.107	
Mass fraction of YSZ	8.804E-05	
Mass fraction of Ni	0.0001513	
Area of carrier	0.0062917	m2
Area of pore	3.14E-10	m2
No of pores per unit volume	1.505E+11	
Effective porosity	0.463	
Porosity of cathode	0.5	
Diffusivity of hydrogen	8.22E-05	m2/s
Diffusivity of oxygen	0.0008951	m2/s
Diffusivity of oxygen in nitrogen	0.0017667	m2/s
Effective diffusivity	8.487E-05	m2/s
Resistance due to electrons	0	
Resistance due to electrolyte	0.29	ohm.m
Equilibrium Voltage	1.1	V
Diameter of Nickel particle (w time)	1.498E-06	m
Partial pressure of H2	98261	Pa
Partial pressure of H2O	3039	Pa
Temperature	1123	K
Time(In hours)	1	
Time in hours		
k3	0.0001488	

0.2 micron? Assuming the initial reduction process yields approximately same size particles as the oxide

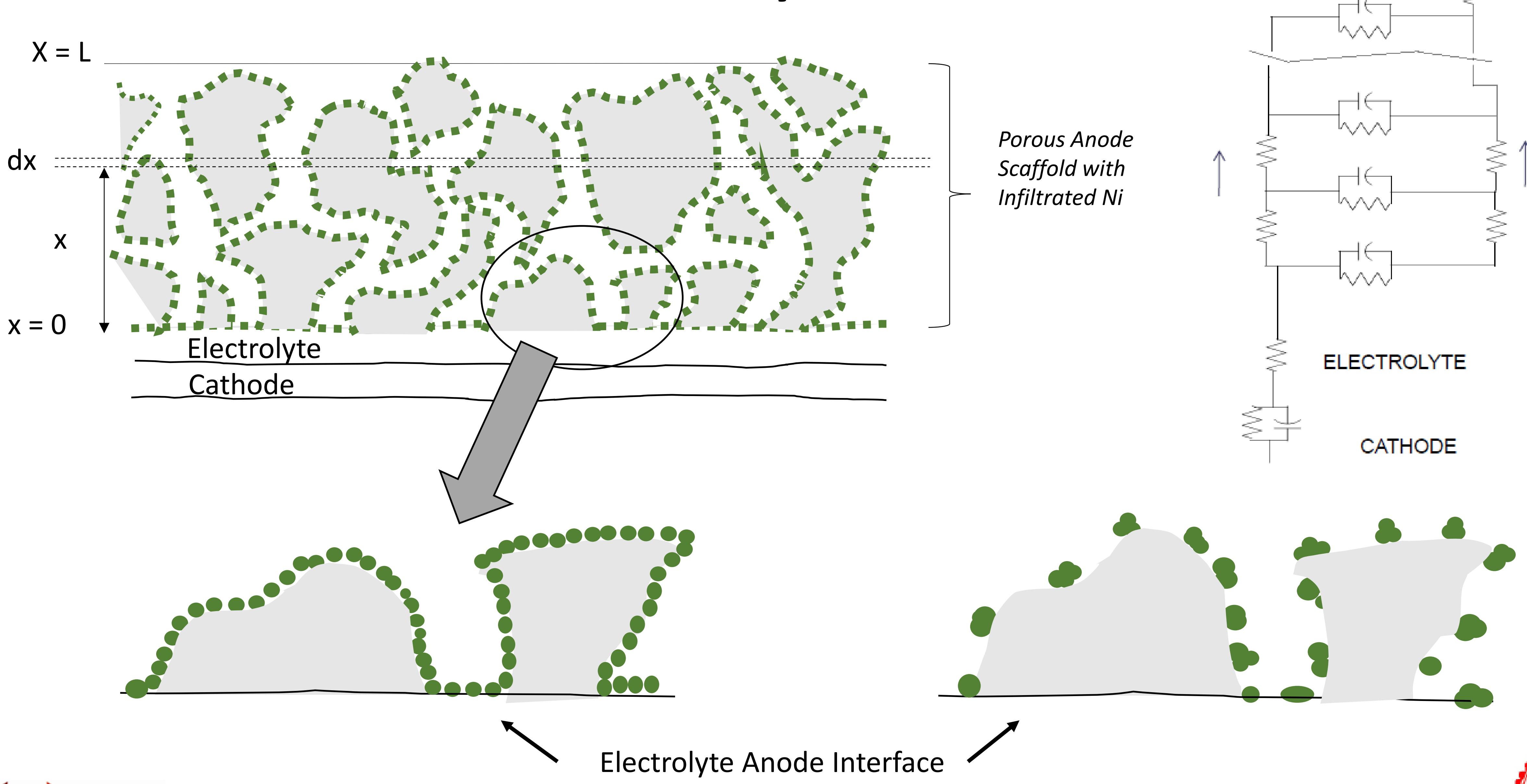
Predicted I-V curve; as function of **tortuosity factor**; 850 deg. C, starting d_{Ni} ~ 200 nm, Porosity = 0.57; Comparison w exptl data



L_{tpb} inversely proportional to Tortuosity factor

Not much progress in predicting performance here.

Situation: Where ionic conductivity within anode matters



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EXTENDED TPB

- Cathodic Loss: $\eta = \frac{RT}{F}\sinh^{-1}\left(\frac{j}{2j_0}\right)$
- Electrolytic Loss: $\eta_{ohmic} = IR_{electrolyte}$
- Anodic Loss:

$$\delta\eta_{anode} = -(\delta\eta_{act,anode} + \delta\eta_{ohmic,anode}) = -(\delta\eta_{act,anode} + \delta\eta_{ohmic,e,anode} + \delta\eta_{ohmic,i,anode})$$

$$= -\delta\left[\frac{RT}{F}\sinh^{-1}\left(\frac{j_e}{2j_{0'}l_{tpb}}\right)\right] - \delta(i_e R_e) - \delta(i_i R_i)$$

We have 2 types of charge carriers in the body of the anode – the oxide ion and the electron

$$ltpb = f(\varepsilon, \tau, L, d_p, d_{Ni}, \theta_{Ni-YSZ}) = k\varepsilon\left[\frac{1}{4\tau L} + \frac{1}{d_p}\right]$$

- Cell Voltage:

$$V_L = E_{Nernst} - (\eta_{cathode} + IR_{electrolyte}) - \int_0^L \delta\eta(x)_{anode}$$

MODEL EQUATIONS:

- The voltage loss occurring in a finite element and current produced are given by the following equations:

$$1.dV = -\left[d\left(R_e j_e + R_i j_i\right) + \frac{RT}{F}\frac{1}{\sqrt{\left(\frac{j}{2 j_{0'} l_{tpb}}\right)^2 + 1}}\, dj \right]$$

$$j_e + j_i = I$$

$$2.\frac{dJ_{H_2}}{dx} = -(reaction.rate_{volumetric})$$

$$\frac{D_{H_2}}{RT}\frac{d^2 p_{H_2}}{dx^2} = l_{v,tpb}\left[k_3\theta_H\theta_{OH} - k_{-3}\theta_{H_2O}(1-\theta_H)\right]$$

$$3.\frac{dj_e}{dx} = 2FAl_{v,tpb}\left[k_3\theta_H\theta_{OH} - k_{-3}\theta_{H_2O}(1-\theta_H)\right]$$

$$\theta_H = \frac{\sqrt{K_1 p_{H_2}}}{1+\sqrt{K_1 p_{H_2}}}$$

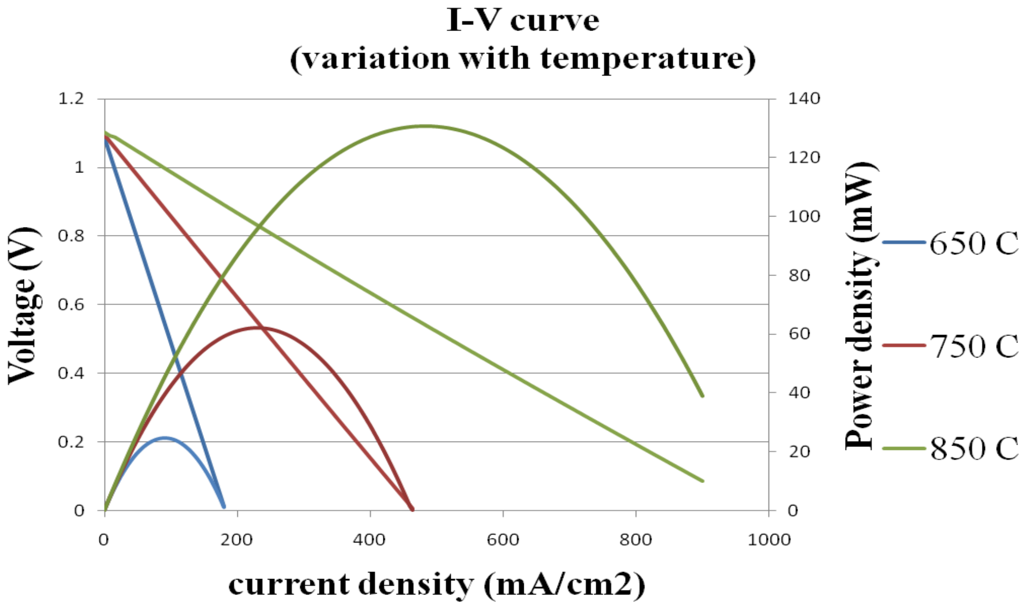
$$\theta_O = \frac{\dfrac{K_5 K_4}{p_{H_2O} + K_4}}{1 + K_5 + \dfrac{K_2 K_5 \theta_H}{1-\theta_H} - K_5\left(\dfrac{\dfrac{K_2\theta_H}{1-\theta_H} + 1}{\dfrac{K4}{p_{H_2O}} + 1}\right)}$$

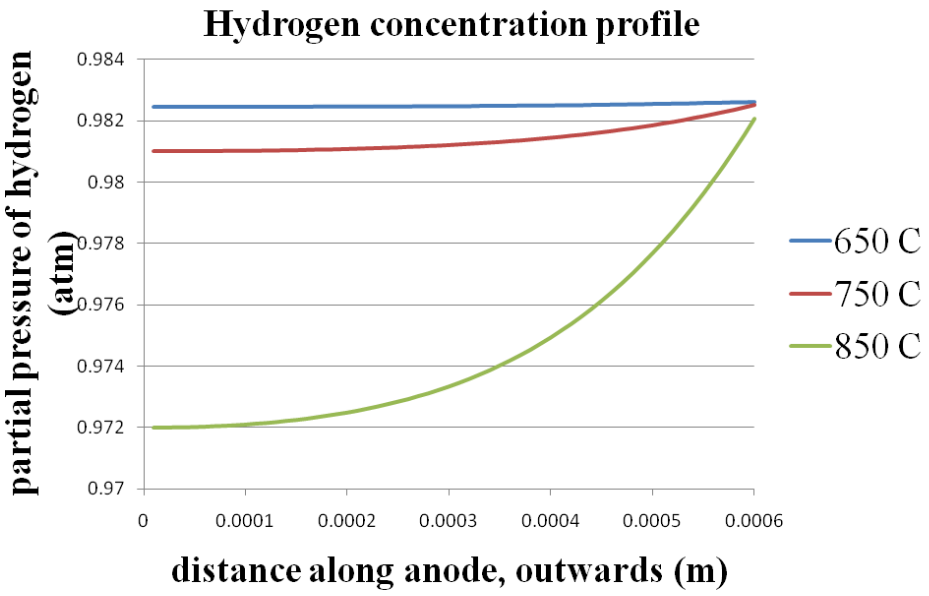
$$\theta_{OH} = \frac{K_2\theta_H\theta_O}{1-\theta_H}$$

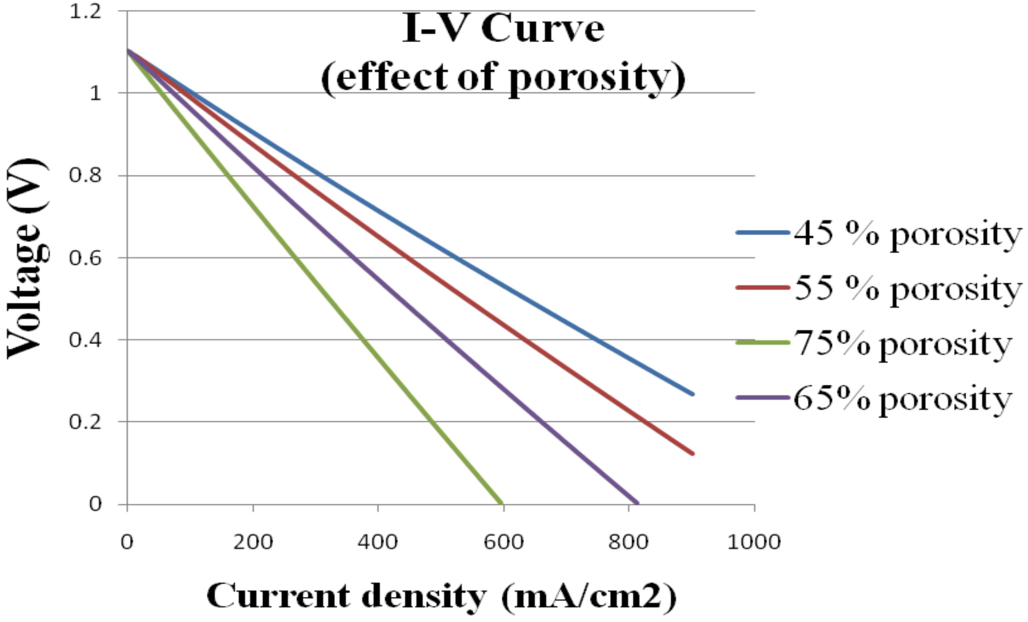
$$\theta_{H_2O} = \left(\frac{1 - \left[\dfrac{K_2\theta_H}{1-\theta_H} + 1\right]\theta_O}{\dfrac{K4}{p_{H_2O}} + 1}\right)$$

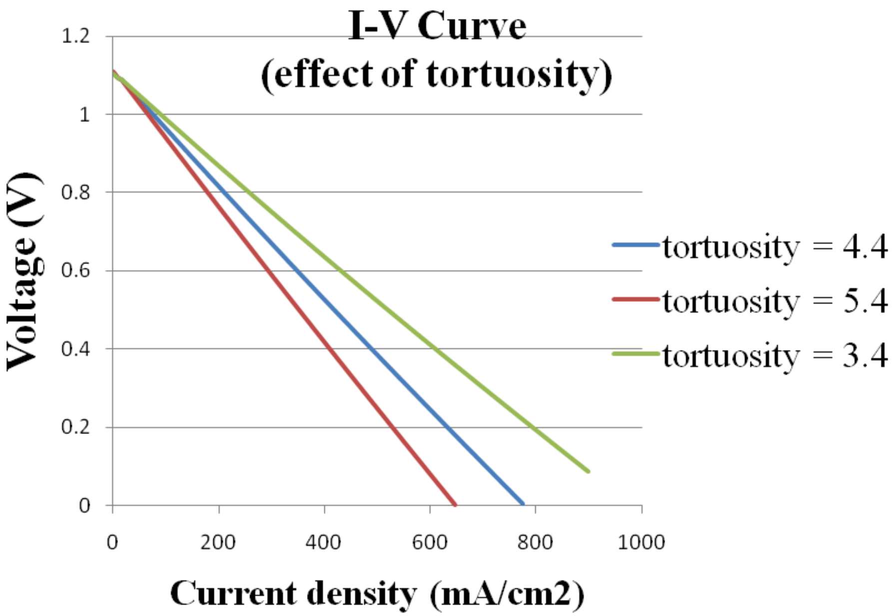
$$p_{H_2O} = p^0_{H_2O} + (p^0_{H_2} - p_{H_2})$$

PREDICTED PERFORMANCE CURVES

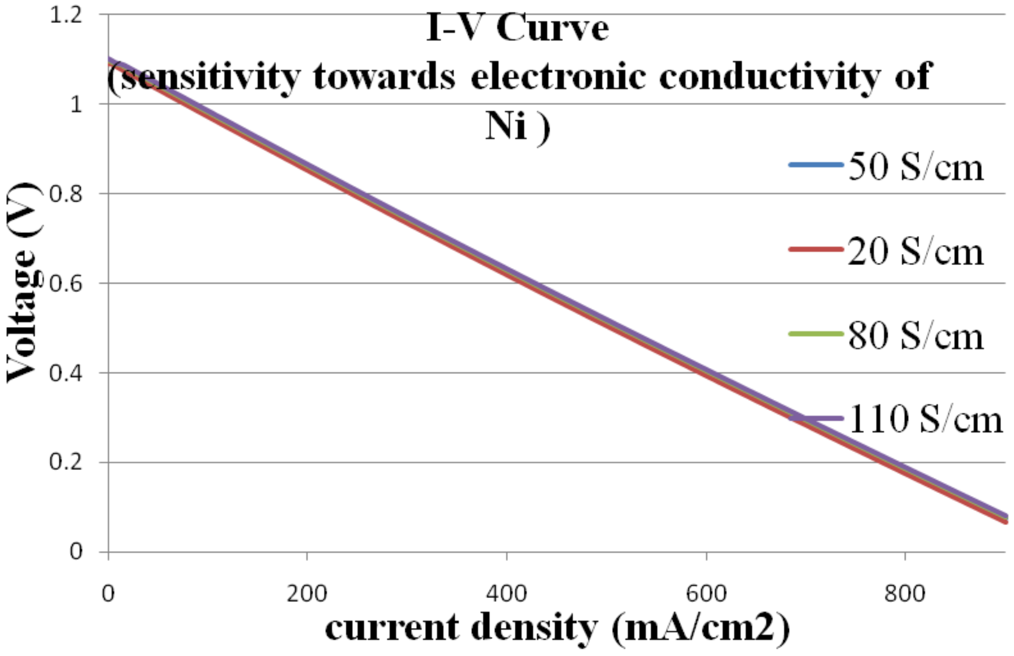


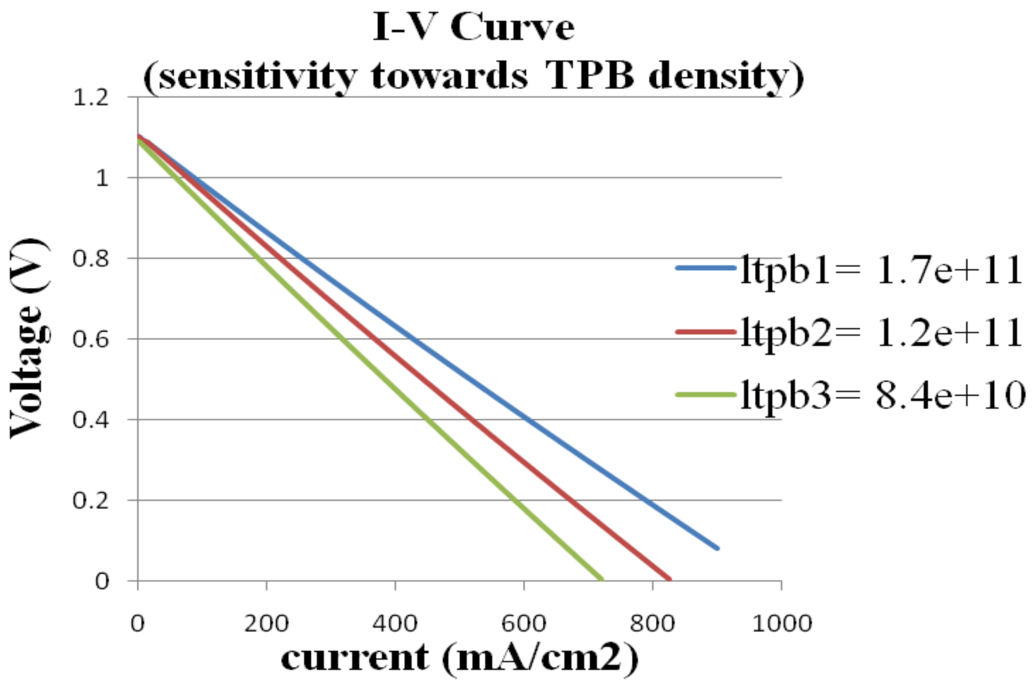




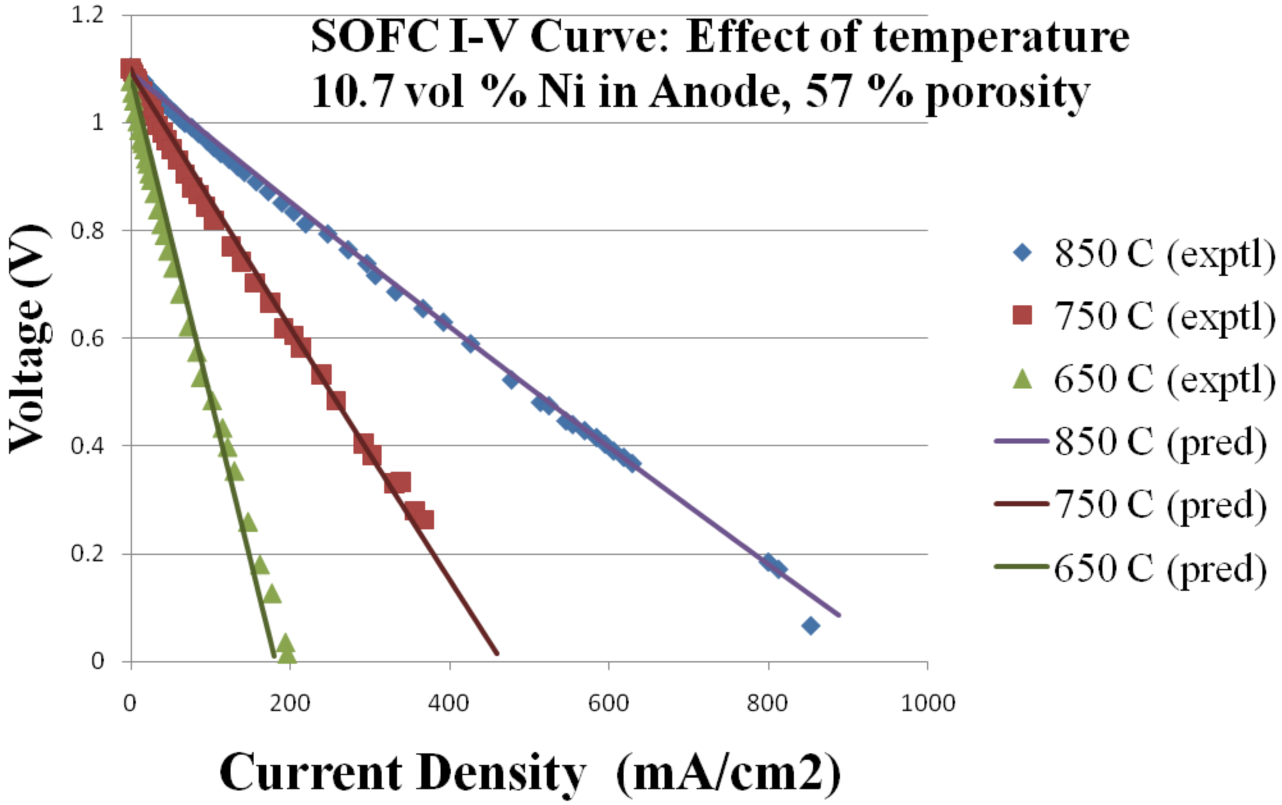


Parametric sensitivity analysis (cont'd)



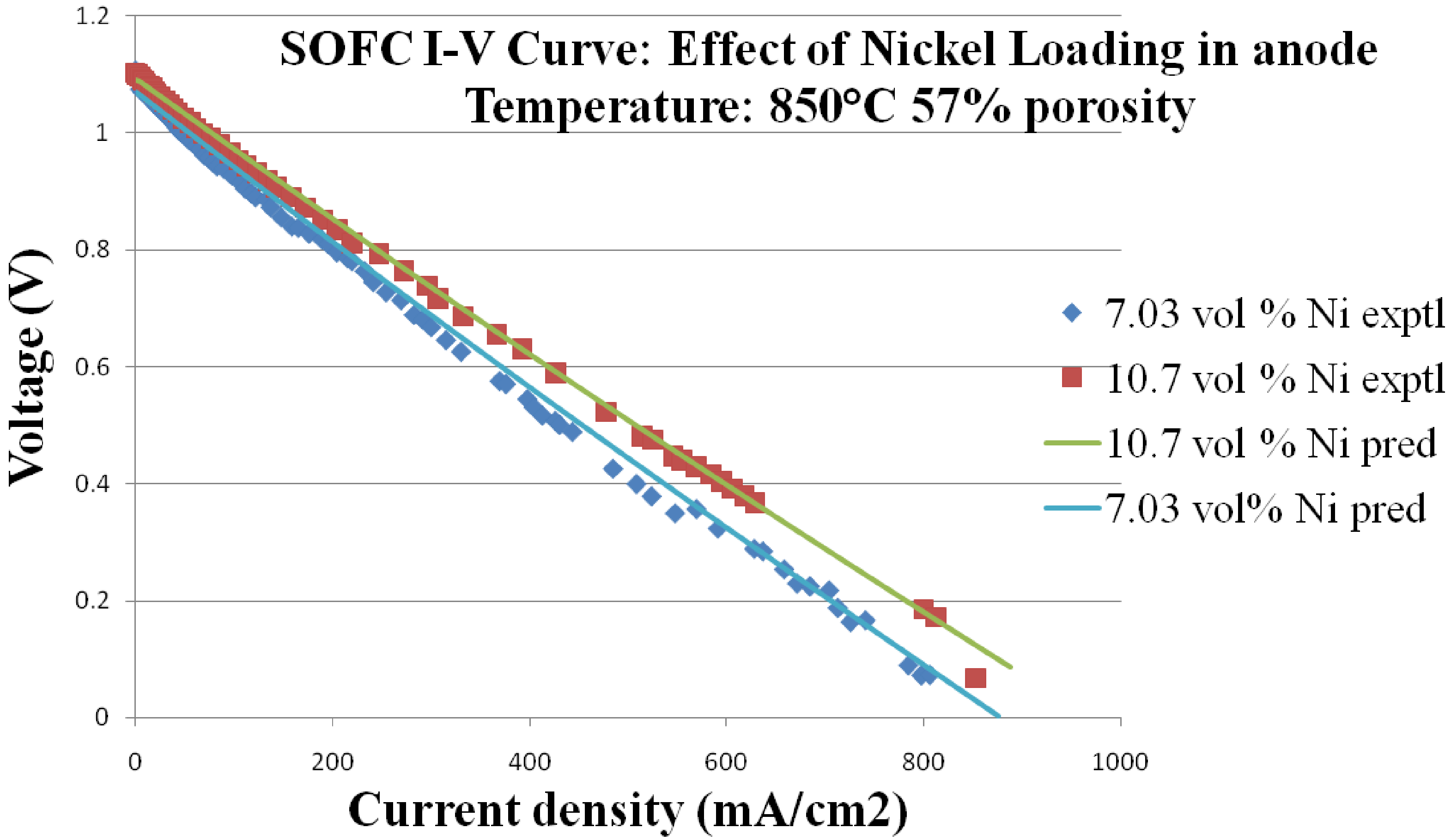


Model Validation: Curve-fitting of experimental data



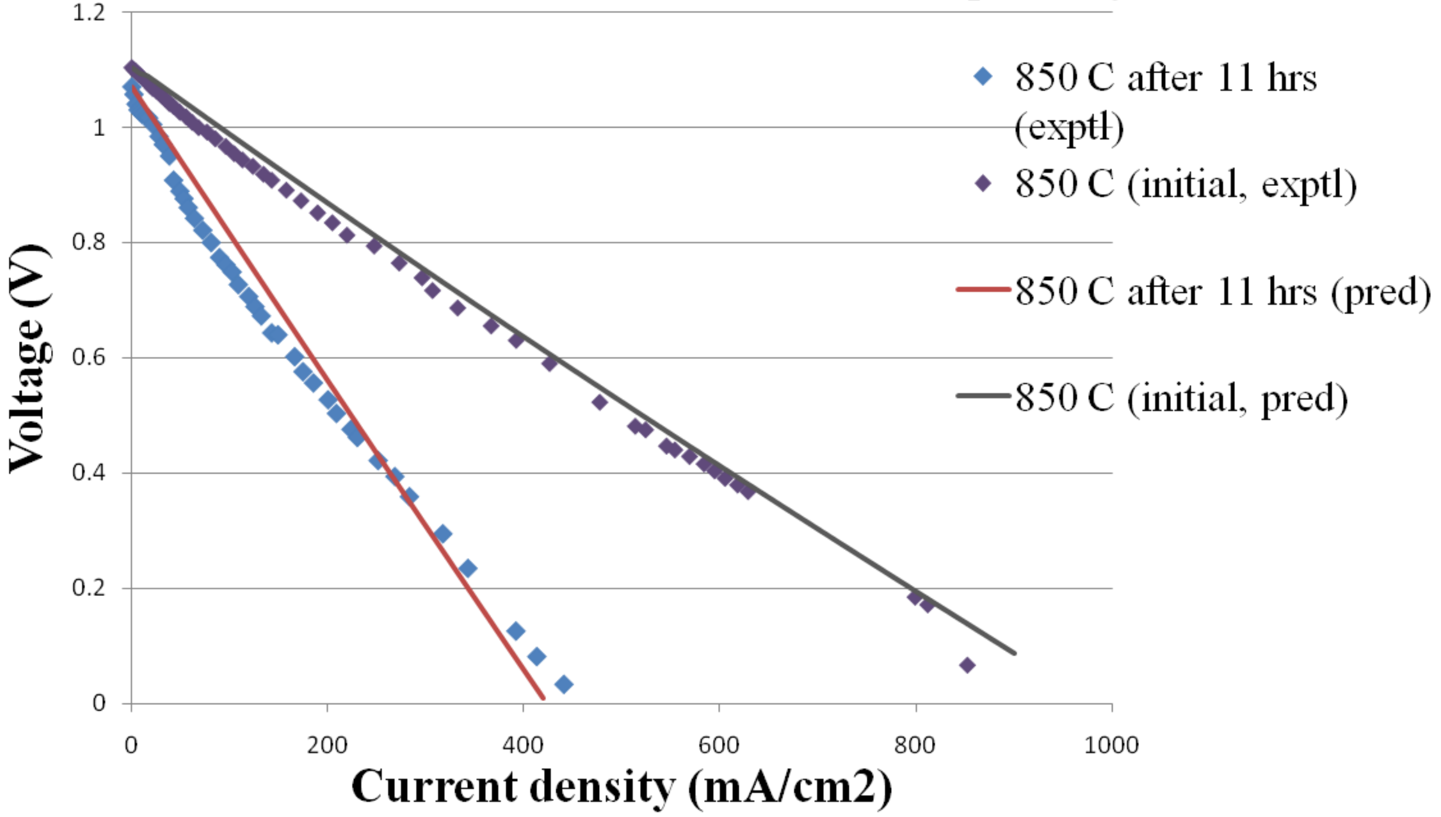
TEMPERATURE (°C)	TPB DENSITY (m/m^3)
650	$3.1*10^{11}$
750	$2.8*10^{11}$
850	$1.7* 10^{11}$

SOFC I-V Curve: Effect of Nickel Loading in anode
Temperature: 850°C 57% porosity



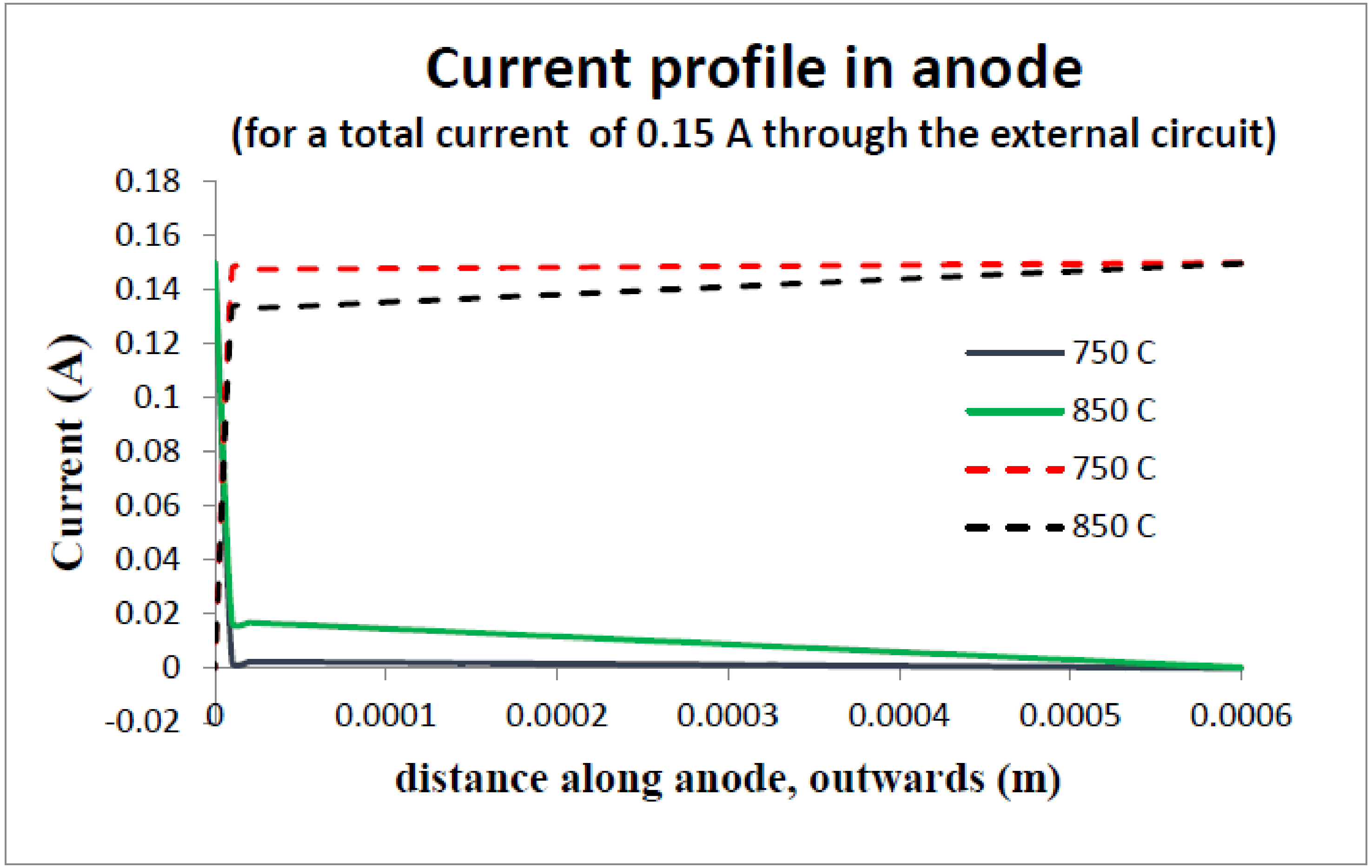
NICKEL LOADING (Vol %)	TPB DENSITY (m/m^3)
10.7	1.7* 10^{11}
7.03	1.2*10^{11}

SOFC I-V Curve: Effect of time
10.7 vol% Ni in anode, 57% porosity



TIME (hrs)	TPB DENSITY (m/m^3)
0 (initial)	1.7* 10^{11}
11	5.1*10^{10}

Current Profiles do exist, within the anode, over a small region – yet to be predicted with accuracy



In future, to be verified by EIS data – may lead to an enhancement in Ohmic contribution due to ionic current in the anode

Figure 13: Current profiles in anode (Ionic vs Electronic); Total current = 0.15 A

Summary of Curve Fits

- Broadly, the utilization of ionic and electronic currents in the anode, enables us to have better curve fits
- 3 phase boundary estimates are within the order of magnitude, reported by many researchers – via direct imaging and counting using rigorous software. Errors and inaccuracies can be minimized by taking into account particle size distribution and pore size distribution
- Very difficult to measure tortuosity although at IITD, (2008-10), we did have estimates by using a diffusion apparatus
- Exact starting point of Ni particle diameter is unclear here – NiO→Ni occurs from 400 C; cells operate at 650 and above, by which time we have a combination of NiO reduction and Ni sintering; this adds to the errors in curve-fitting cell performance
- It is clear – that Ni coarsening has a stronger influence on 3 phase boundary and very less on overall anodic electronic conductivity, which seems to be largely stable – as showed in our electrical conductivity data
- Refinement of model w.r.t kinetics, and extension of model for conventional NiO-YSZ anodes is in progress (a similar Ni sintering model can be used in conjunction with percolation theory – understanding the degradation mechanisms in more hostile environments, i.e., Steam Electrolyzers

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